

## Molecular Tribometry of Ultrathin Liquid Films

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(Received 15 September 1988)

We study the resistance to sliding of liquid films 1–6 molecules thick. The apparent dynamic viscosity at 1 Hz of nonpolar liquids confined between parallel plates of atomically smooth mica is considerably enhanced over that of the isotropic fluids and shows extreme dependence on pressure. Rapid, reversible switching between liquidlike and noncompliant responses as a function of small changes in normal pressure is also found, suggesting a phase transition to a solidlike structure.

PACS numbers: 68.45.-v, 47.25.Ei, 62.20.Pn, 82.65.Dp

What is the structure of liquid near a boundary? The question of the order imposed on liquids by proximity to a surface is now of emerging interest in studies of force-distance profiles between surfaces in liquids,<sup>1</sup> of physics of liquids in porous media,<sup>2</sup> and of wall-induced orientational ordering of liquid crystals.<sup>3</sup> The issues raised are also clearly relevant to many other diverse physical phenomena, among them the stability of colloids, the no-slip condition of continuum hydrodynamics, and lubrication.

In this Letter, we describe what we believe to be the first study of the dynamic oscillatory shear response of liquid films so thin that their thickness is comparable to molecular dimensions. The results raise many questions concerning the packing and crowding of fluid molecules in constricted geometries. In particular, we find that the energy dissipation in sinusoidal shear oscillation between parallel plates is considerably enhanced over that of the isotropic fluid. It shows a remarkable dependence on pressure. A phase transition to a solidlike state is suggested.

The molecular tribometer shown schematically in Fig. 1 was constructed. A home-built force balance ap-

paratus<sup>4</sup> was modified so that two sheets of muscovite mica, coated onto cylindrical silica lenses and positioned at right angles to one another, can be sheared at constant separation. Shear is induced with use of piezoelectric elements. Surface separation and normal load are controlled by a micrometer-driven drive. The bottom mica-coated lens is mounted onto the tip of a double cantilever leaf spring whose fulcrum is attached to the micrometer drive. The top mica-coated lens is mounted to a small boat rigidly attached to two piezoelectric bimorph strips, mounted symmetrically. Shear is induced when the sinusoidal output from a function generator tends to bend one bimorph. Viscous dissipation resists this motion, and the actual displacement is sensed by the receiver bimorph. After amplifying, digitizing, and signal averaging, the experimental waveforms are transferred to a personal computer and the amplitude attenuation and phase shift of the receiver signal are determined by cross correlation. Viscous energy dissipation is then calculated from the out-of-phase component of the response. Changes in surface separation are measured to  $\pm 2 \text{ \AA}$  by optical interferometry between the back sides

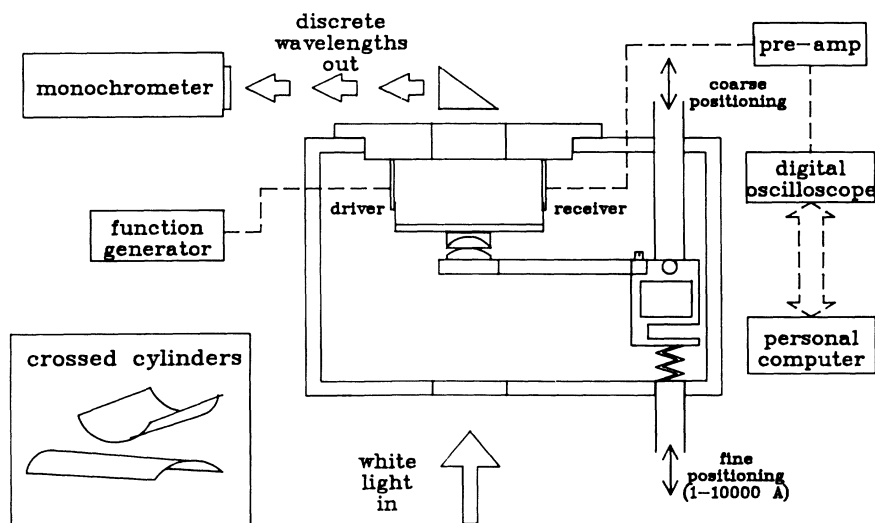


FIG. 1. Schematic diagram of the molecular tribometer.

of the mica sheets and refer to the zero measured in dry nitrogen atmosphere. The temperature was  $23 \pm 1^\circ\text{C}$ .

Explanation is needed of the method used to create parallel-plate geometry. The usual force balance experiment measures an interaction between two smoothly curved crossed mica cylinders. However, as the cylinders separated by a liquid droplet are pressed together, the fluid in the final few molecular layers resists being squeezed out. In these experiments, a soft glue (symdi-phenylcarbazide) underneath the mica sheets deformed instead. This resulted in a circular area of constant separation over which nearly all ( $>99\%$ ) of the viscous drag occurred.<sup>5</sup> Contact diameters (measured to  $\pm 5 \mu\text{m}$ ) were typically on the order of  $100 \mu\text{m}$ .

The liquids studied were freshly distilled and stored over type-4A molecular sieves. Immediately before use, they were filtered through an  $0.5\text{-}\mu\text{m}$  Teflon filter. A liquid droplet was placed between the mounted mica sheets. The enclosed and sealed measurement apparatus was purged with dry nitrogen and phosphorous pentoxide was kept inside to scavenge rogue moisture during the experiment.

As the mica cylinders separated by a hexadecane droplet were pushed together, fluid drained smoothly until oscillatory forces of alternate attraction and repulsion were first detected at thickness  $50 \text{ \AA}$ , in good agreement with results of a previous study.<sup>6</sup> These forces arise from the tendency of fluid to form layers parallel to the surface.<sup>1,6</sup> In this range of separation, the film thickness was an integral multiple of  $4 \text{ \AA}$ . Application of pressure caused the fluid to drain in discrete steps corresponding to squeezing out of successive molecular layers.

First we discuss the viscous shear response: the component of the stress at  $1 \text{ Hz}$  which was in phase with the rate of strain. Although these ultrathin fluids were surely inhomogeneous even with respect to density in the nor-

mal direction,<sup>1,6</sup> for want of a better way to represent the data we report it, assuming well-known continuum relations, as an apparent dynamic viscosity ( $\mu'_{\text{app}}$ ). In Figs. 2 and 3, this viscosity is plotted for two amplitudes of sinusoidal oscillation,  $200$  and  $1000 \text{ \AA}$  peak to peak. There is no discernible dependence on amplitude, indicating that the maximum dissipative wall shear stress increased linearly with the maximum velocity of motion.

In this restricted geometry, the apparent viscosity was always larger than that of the bulk liquid. The first film thickness at which parallel-plate geometry was reached was  $D=24 \text{ \AA}$  for the experiment shown in Figs. 2 and 3. At this thickness,  $\mu'_{\text{app}}=0.67 \text{ P}$ , already larger than the  $0.03 \text{ P}$  of bulk hexadecane. As the normal pressure was raised and fluid drained out,  $\mu'_{\text{app}}$  at first increased. This is qualitatively reasonable since at  $D < 24 \text{ \AA}$  the hexadecane molecule is restricted to a space thinner than its contour length of  $23 \text{ \AA}$ .

An extreme influence of normal pressure on the  $\mu'_{\text{app}}$ , with associated changes in film thickness too small to measure, was more surprising. Near each data point in Fig. 2, a number denotes the measured thickness of the liquid film at that normal pressure. For clarity, the data of Fig. 2 are replotted in Fig. 3 to show directly the variation of  $\mu_{\text{app}}$  with film thickness. For a film two molecules thick ( $D=8 \text{ \AA}$ ), one sees that  $\mu'_{\text{app}}$  quintupled as the normal pressure was raised from  $6$  to  $14 \text{ MPa}$ , to give a largest value of  $\mu'_{\text{app}}$  4 orders of magnitude larger than that of bulk hexadecane. If an activation volume is calculated, the result of  $3000 \text{ \AA}^3$  is larger than the volume of a single molecule, suggesting that the unit process involves many molecules. It is as if the molecules were becoming logjammed.

By way of comparison, the viscosity of bulk hexadecane over this range of pressure increases by a factor less than 2. The finding that  $\mu'_{\text{app}}$  depended strongly on pres-

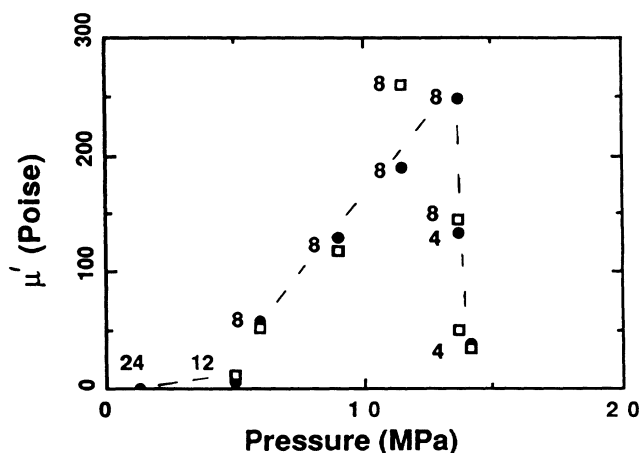


FIG. 2. Apparent dynamic shear viscosity of hexadecane plotted against pressure in the normal direction. Numbers specify film thickness. Amplitude of oscillation:  $200 \text{ \AA}$  (squares) or  $1000 \text{ \AA}$  (circles).

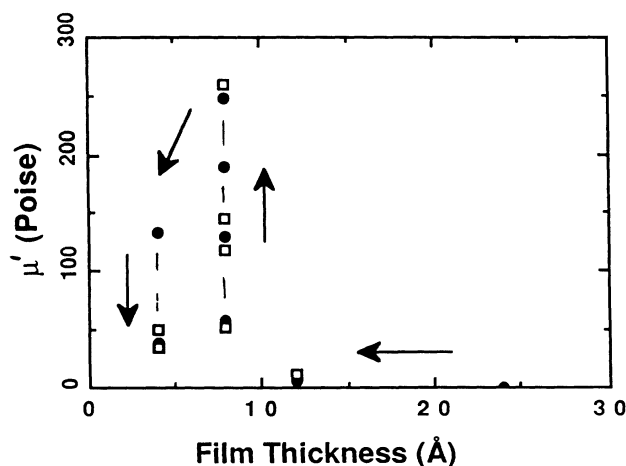


FIG. 3. Apparent dynamic shear viscosity of hexadecane plotted against film thickness. Symbols same as in Fig. 2. Arrows denote direction of increasing normal pressure.

sure as well as on film thickness, under the conditions of this experiment, contrasts with a previous study reporting that the dynamic friction, which succeeds static friction in steady shear flow, was "quantized" according to film thickness only.<sup>7</sup>

In other experiments, such an increase of  $\mu'_{app}$  without discernible change in film thickness was also observed at larger thickness, up to 24 Å. This was very sensitive to experimental details. Vibrations in the laboratory or a rapid rate of pressure increase tended to promote drainage instead of this type of behavior.

An elastic response to shear stress further thickens the plot of this complex story. Further studies are in progress of the curious phenomena that  $\mu'_{app}$  of hexadecane and also of other fluids which were studied (see below) eventually decreased with normal pressure. However, the limit of this phenomenon is clear. At sufficiently large normal pressure these ultrathin fluid layers appeared to respond entirely elastically, in the sense that sliding would not occur unless a finite critical shear stress was exceeded. This is discussed further below.

The generality of these findings was tested. It should be noted that the freezing temperature ( $T_m$ ) of isotropic hexadecane is 18°C at 1 atm and may be expected<sup>8</sup> to be raised 3°C at our largest pressure. This raised obvious questions, and accordingly similar shear measurements were also made of decane (also chainlike,  $T_m=30^\circ\text{C}$ ) and of the cyclic dimethylsiloxane tetramer, octamethylcyclo-tetrasiloxane (OMCTS), globular shape,  $T_m=17^\circ\text{C}$ ). Force-distance profiles are known.<sup>6,9</sup> The results (not shown) were qualitatively similar to those shown above for hexadecane, despite significantly different  $T_m$  (decane) and molecular shape (OMCTS). In particular, the solidlike response referred to above was observed.

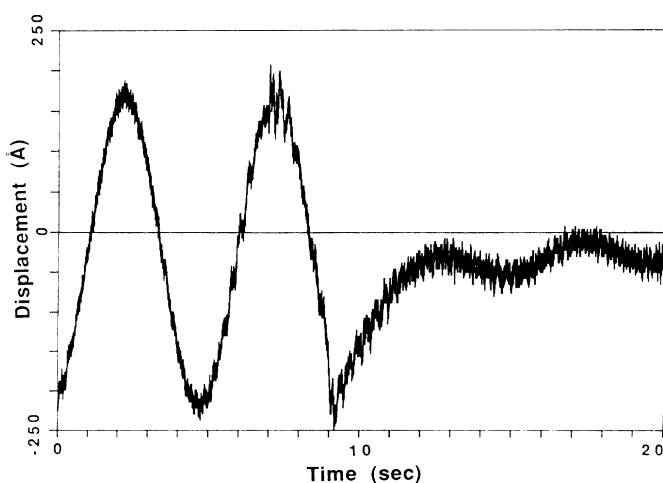


FIG. 4. Oscilloscope trace of the amplitude of oscillation plotted vs elapsed time, for the shear of an OMCTS film as described in text. Noise is 60-Hz vibration.

The rapid switching one could observe between liquidlike and solidlike responses is illustrated in Fig. 4 for an experiment with OMCTS. The actual amplitude of oscillation during an experiment at 0.2 Hz is plotted against the elapsed time in data taken from an oscilloscope trace. The film thickness was two layers (18 Å) and the normal pressure was 3.6 MPa. A compliant response ( $\mu'_{app}=540\text{ P}$ ), on the left-hand side of Fig. 4, switched abruptly to a response characteristic only of the experimental apparatus (the mica and its underlying glue). As noted above, separate experiments where the amplitude of shear force was varied showed that in this state a critical shear stress was required to initiate sliding. This stress was directly proportional to the normal pressure, at constant film thickness, similar to the pressure dependence noted above for  $\mu'_{app}$ . Transitions to the solidlike response were observed in films of thickness corresponding to one, two, or three molecular layers. The systems appeared to be unstable, when the pressure was high, between the solidlike state and drainage of liquid.

In Fig. 4, note that the transition occurred in the space of less than 5 s. The transition was reversible if the normal pressure was lowered (or subsequently raised) by small amounts, ca. 0.01 MPa. It cannot be ruled out that the transition involved forming a glass, but its rapidity and reversibility are striking and suggest a first-order transition.

Does this solidlike response reflect a static structure (perhaps induced by the walls or by molecular packing) or was it induced by shear? Although shear may have contributed sometimes, it is clear experimentally that the solidlike response did not degrade with time after it appeared, even though motion was quenched. Also, when shear was initiated starting at a high normal pressure, the solidlike response was observed right from the start. On the other hand, the possibility of surface-induced epitaxial crystallization, suggested by molecular-dynamics studies of Lennard-Jones fluids in pores,<sup>10</sup> may not explain these experimental findings either. To observe similar results for OMCTS as for the linear alkanes suggests that these findings do not originate in coincidental commensurability between the liquid microstructure and that of the mica walls, but may be representative of more generic features of the packing of constricted nonspherical liquids.

In summary, we have identified two qualitatively different responses to shear of these inhomogeneous, ultrathin films. In one response, no critical shear stress was required for motion. The apparent dynamic viscosity was considerably enhanced over that of the isotropic fluid and showed extreme dependence on pressure. However, rapid, reversible switching to a solidlike response was also observed. Among the experimental questions that are open at present are a firm identification of what underlying structure is equilibrated and what is metastable, and elucidation of the actual structure of these

strange constricted mesostates. These results broach an unexpectedly rich physics when the thickness of a fluid film approaches molecular dimensions.

We thank J. D. Ferry and Y. Oono for comments. This work was supported by a Grant, No. MSM-85-19349, from the Tribology Program of the National Science Foundation, with assistance from the 3M and IBM Corporations.

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